

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/EP05/002889

International filing date: 17 March 2005 (17.03.2005)

Document type: Certified copy of priority document

Document details: Country/Office: DE
Number: 10 2004 013 634.3
Filing date: 18 March 2004 (18.03.2004)

Date of receipt at the International Bureau: 26 April 2005 (26.04.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

BUNDESREPUBLIK DEUTSCHLAND

19.04.2005



EP05/2889

**Prioritätsbescheinigung über die Einreichung
einer Patentanmeldung**

Aktenzeichen: 10 2004 013 634.3

Anmeldetag: 18. März 2004

Anmelder/Inhaber: Ormecon GmbH, 22949 Ammersbek/DE;
Nissan Chemical Industries, Ltd., Tokio/Tokyo/JP.

Bezeichnung: Composition Comprising a Conductive Polymer
in Colloidal Form and Carbon, Process of Manu-
facturing and Use

IPC: C 09 D, C 08 L, C 08 K

Die angehefteten Stücke sind eine richtige und genaue Wiedergabe der ur-
sprünglichen Unterlagen dieser Patentanmeldung.

München, den 06. April 2005
Deutsches Patent- und Markenamt
Der Präsident
Im Auftrag

Stanschus

UEXKÜLL & STOLBERG

PATENTANWÄLTE

BESELERSTRASSE 4
D - 22607 HAMBURG

Ormecon GmbH
Ferdinand-Harten-Str. 7

22949 Ammersbek

Nissan Chemical Industries, Ltd.
Kowa Hitotsubashi Building
11th Floor 7-1,
Kanda-Nishiki-cho
3-chome, Chiyoda-ku

Tokyo 101-0054
Japan

DR. J.-D. FRHR. von UEXKÜLL (- 1992)
DR. ULRICH GRAF STOLBERG (- 1998)
EUROPEAN PATENT ATTORNEYS
EUROPEAN TRADEMARK ATTORNEYS
DIPL.-ING. JÜRGEN SUCHANTKE
DIPL.-ING. ARNULF HUBER
DR. ALLARD von KAMEKE
DIPL.-BIOL. INGEBORG VOELKER
DR. PETER FRANCK
DR. GEORG BOTH
DR. ULRICH-MARIA GROSS
DR. HELMUT von HEESCH
DR. JOHANNES AHME
DR. HEINZ-PETER MUTH
DR. MARTIN WEBER-QUITZAU
DR. BERND JANSSEN
DR. ALBRECHT von MENGES
DR. MARTIN NOHLEN
MÜNCHEN
DIPL.-ING. LARS MANKE
DR. OLGA BEZZUBOVA
RECHTSANWÄLTE IN HAMBURG
DR. FRANK DETTMANN
ASKAN DEUTSCH, LL.M.

18. 3. 2004
P 65623 No/pz

**Composition Comprising a Conductive Polymer in Colloidal Form and Carbon,
Process of Manufacturing and Use**

Conductive Materials are known and used in many different forms and applications. Conductive materials based on carbon are available in several different physical and chemical morphology, form and composition. Pure or mainly pure carbon is available in the form of carbon black (which contains also mainly oxygen based in purity), graphite (pure), carbon nanotubes and fullerenes and others. Carbon based organic compounds are available in form of (intrinsically) conductive polymers which have found some first applications. These various different types of carbon based conductive materials have at least one property in common, the conductivity, and other properties may be exclusive to the one or the other representative of this group of materials or may vary widely, like particle size (graphite in the range of several to

several 10 μm , fullerenes in the range of angstroms), specific surface (carbon black and carbon nanotubes having high values up to about 1000 m^2/g , graphite having low values only in the range of a few m^2/g) or redox chemistry (polyaniline, one of the representatives of conductive polymers, exhibiting a rich redox chemistry, PEDT or PEDOT (polyethylenedioxythiophene), a moderately or pure redox chemistry, and on the other side graphite or carbon black (no reversible redox chemistry)).

Therefore, it is sometimes of interest to combine materials with widely varying properties in order to provide a combination of properties which otherwise would not be accessible.

The combination of conductive polymers like polyaniline, polyethylenedioxythiophene, polypyrroles or their derivatives with carbonaceous materials (carbon black, graphite, carbon nanotubes and fullerenes) has sometimes been tried. Whereby simple mixtures of said materials do not offer any significant or reproducible advantage and hence did not find any commercial or technological attractiveness, chemical processes for the combination of for instance conductive polymers and carbon black or conductive polymers and carbon nanotubes have been widely studied. For instance, the company Eeonyx has offered carbon black on which surface polyaniline was polymerised as a developmental product in the market ("Eeonomer"), cf. G. Du, A. Epstein, K. Reimer, presentation on the March 1996 Meeting of the American Physical Society, Session M23, presentation M 23.09; the laboratory chemicals supplier Aldrich has advertised such a chemically produced mixture in their catalogue. However, obviously such a product did not offer interesting advantages.

One of the areas in which carbon black polyaniline mixtures could offer an interesting technological advantage, could be the area of so called 'supercapacitors', also often called 'double layer' or 'redox capacitors'. This area provides the highest number of publications in which carbon and conductive polymers have been mixed or provided in form of a mixture.

For this purpose, principally two mixing procedures have been used:

- 5 - Simple mixing of powders of carbon black and polyaniline by one day of ball milling (US-Patent Application 2002/0114128) or in other form (no description given, Journal of Power Sources 11, 2003, 185-190, and Journal of the Electrochemical Society, 148, 10, 2001, A1130-A1134), where polyaniline or a polythiophene derivative were mixed with carbon black powders.
- 10 - Chemical or electrochemical polymerisation of different conductive polymers on the carbon black surface.

The latter method has been widely investigated in the patent and scientific literature. European Patent Application EP 1 329 918 reports about a negative electrode composite of carbon and polyaniline or polypyrrole in which the conductive polymer
15 was electrochemically polymerised. The positive electrode was made from lead. The conductive polymer content was found to be optimal at 10–15% by weight. The capacitor formed using this mass was made by an electrode combination which includes a positive non-polarisable and a negative polarizable electrode whereby the positive non-polarisable electrode was made from lead. US Patent Application
20 2002/0089807 reports about an intrinsically conductive polymer directly polymerised on highly porous carbon black material by chemical or electrochemical means. By electrochemical polymerisation, polyaniline was polymerised on a carbon aerogel, generated from polyacrylonitrile (Journal of Applied Electrochemistry 33, 465-473, 2003), comparable to the electrochemical polymerisation of Pani on active porous
25 carbon (Journal of Power Sources 117, 273-282, 2003 and lit. 10, Carbon 41, 2865-2871, 2003). In Conference Proceedings of ANTEC '98, Vol. 2, 1197ff, 1998, the authors report about the polymerisation of polyethylenedioxythiophene on high surface area films of carbon on a platinum current collector support. In the same publication it was reported that polyaniline was cast from hexafluoro-isopropanol
30 solutions on the same type of carbon films.

In *Electrochimica Acta* Vol. 41, No. 1, 21-26, 1996 it was reported about various redox supercapacitors in symmetry or non-symmetric electrode configuration form in which various conductive polymers like polypyrrole or polythiophene derivatives have been used and polymerised on the substrate, in a comparable procedure as used in US-Patent 5,527,640, 1996, where polythiophene derivatives were polymerised on carbon substrates by electrochemical means.

[Detailed Description of the Invention]

10 [Technical Field to which the Invention Pertains]

The present invention relates to conductive materials composed from (intrinsically) conductive polymers and carbon based materials, methods for their manufacture and use for a high-capacity electrical double layer capacitors to be utilized in various electronic apparatuses, power devices and the like.

15

[Prior Art]

As explained above, carbon black / conductive polymer mixtures have often been prepared for use in so-called "supercapacitors". Such capacitors are also often referred to as "double layer capacitors", "electrochemical" or "electrical double layer capacitors" or "redox capacitors" as well as sometimes "pseudo-capacity capacitors".

20

Conventionally, a double layer capacitor is an energy device in which two electrodes - at least one of which obtained by coating a collector plate with a porous carbonaceous material having a high specific surface area between and above about 100 and 1000 m²/g to a collector plate - are opposed to each other with a separator disposed therebetween, a voltage is impressed on the electrodes in the presence of an electrolyte solution, to generate an electrical double layer on at least one of the electrodes, and energy can be taken out therefrom. The structure of one kind of double layer capacitor using the porous carbonaceous material as electrode material is, as disclosed in the specification and drawings of US Patent No. 5150283, classified into the type in which a pair of electrical double layer electrodes (each comprising a

25

30

polarizable electrode joined to a collector plate) are wound and contained in a container and the button type in which a pair of electrical double layer electrodes are laminated.

5 The wound type has a configuration in which a lead wire for taking out energy to the exterior is attached to a collector plate composed, for example, of an etched aluminum foil with a thickness of 20 to 50 μm , the aluminum foil is coated with a paste composed of a mixture powder prepared by admixing an active carbon powder with a desired binder and a desired conductive agent to form a conductive layer, a
10 polarizable electrode composed of an active carbon layer consisting mainly of active carbon is formed on the conductive layer to obtain an electrical double layer electrode, and a pair of such electrical double layer electrodes are opposed to each other with a separator disposed therebetween and are wound.

15 In addition, the electrical double layer electrodes are assembled by a method in which the polarizable electrode composed of the active carbon layers and the separator are sufficiently impregnated with an electrolytic solution containing an electrolyte dissolved therein under vacuum, the electrodes and the separator are inserted into a case made of aluminum or the like, and an opening portion of the aluminum case is
20 sealed by use of a packing. Generally, this assembly is of a cylinder type.

On the other hand, the button type has a structure in which a polarizable electrode composed of an active carbon layer is formed on a disk form sheet of a valve metal to obtain an electrical double layer electrode, and a pair of such electrical
25 double layer electrodes are disposed opposite to each other with an insulating separator therebetween, and this assembly is contained in a metallic container composed of two members. The two electrical double layer electrodes have their disk form sheets (or foils) of valve metal joined respectively to the inner sides of a bottom portion and a top cover portion of the metallic container, the bottom portion and the
30 top cover portion are joined to each other while being hermetically sealed with an insulating ring packing at a circumferential edge portion thereof, and the inside of the

container is filled with a nonaqueous electrolytic solution which is supplied sufficiently to the electrical double layer electrodes and the separator. As the nonaqueous electrolytic solution, for example, a solution prepared by adding tetraethylammonium tetrafluoroborate to propylene carbonate is utilized.

5

There are several other configurations of double layer capacitors or redox capacitors (often called "supercapacitors") in use which will not be described here in detail.

10

There has been proposed a high-capacity electrochemical capacitor in which an electrochemically active inorganic substances or organic (intrinsically) conductive polymers are used as electrode materials in combination with or in place of the above-mentioned porous carbonaceous material and in which electric power storage based on the formation of electrical double layers is utilized, in the same manner as in the ordinary electrical double layer capacitor using the above-mentioned porous carbonaceous material, and, simultaneously, electric power storage based on an oxidation-reduction potential attendant on oxidation-reduction reactions at both electrodes is utilized, to thereby achieve a high capacity.

15

20

For example, an electrochemical capacitor using ruthenium oxide as an electrode active substance (Physics Letters, 26A, p.209 (1968)) is evaluated to be the highest in performance of the electrochemical capacitors using an inorganic oxide known at present, and has been confirmed to have an energy density of 8.3 Wh/kg and an output density of 30 kW/kg.

25

In recent years, capacitors using other inorganic oxide mixture systems as electrode material have been investigated (J. Power Sources, vol. 29, p.355 (1990)).

30

Also, electrochemical capacitors using as electrode material, a so-called (intrinsically) conductive polymer utilizing the oxidation-reduction characteristic of a π -conjugated system organic substance, other than the above-mentioned inorganic metal oxides, have been actively studied in recent years.

The electrochemical capacitors using the conductive polymers have been investigated in many research institutes, and, as to the characteristics, it has been reported that, for example, the use of polypyrrole as electrode material gives a capacity of 86 C/g and an energy density of 11 Wh/kg, the use of a mixture of polypyrrole and polythiophene gives a capacity of 120 C/g and an energy density of 27 Wh/kg, and the use of poly-3-(4-fluorophenyl)thiophene gives a capacity of 52 C/g and an energy density of 39 Wh/kg (J. Power Sources, vol. 47, p.89 (1994)).

Other than the above, in the type of utilizing intercalation for a high-capacity capacitor, generally, a layer structure substance (TiS_2 , MoS_2 , CoO_2 , V_6O_{13}) is used as the electrode material. In this case, the device is in many cases assembled with asymmetric electrodes (Japanese Translations of PCT for Patent Nos. 2002-525864, 2002-542582).

Furthermore, composite materials prepared from the above-mentioned various electrode materials have been evaluated in some cases, to achieve much higher capacities, as compared to the conventional capacitors using only the porous carbonaceous material as an electrode material.

[Problems to be Solved by the Invention]

In spite of intensive research, no mixtures of carbonaceous materials and (intrinsically) conductive polymers are in industrial use. The reasons for this can mainly be found in a poor homogeneity of the mixture on the nanoscopic scale and a poor reproducibility of the properties due to the manufacturing processes (as described above) used.

On the other side, the above-mentioned conventional electrical double layer capacitors using a porous carbonaceous material for polarizable electrodes are limited in capacity, though they are good in quick charge-discharge characteristics. For

example, as described in Japanese Patent Laid-open No. 2003-338437, a capacitor using active carbon (surface area: $650 \text{ m}^2/\text{g}$) obtained by activation of a porous carbonaceous material has an electrostatic capacity of 18.3 F/g , which is lower than those of electrochemical capacitors.

5

As for the relationship between the electrostatic capacity and the specific surface area of the porous carbonaceous material, an electrostatic capacity of about 22 F/cc is obtained when the specific surface area is in the range of 1500 to $2600 \text{ m}^2/\text{g}$, but, when the specific surface area is more than the range, the capacity is not increased any longer but tends to the decreased ("Electrical Double Layer Capacitors and Electric Power Storage Systems", The Nikkan Kogyo Shimbun, Ltd., p.9).

10

Other than the above, further examples of an electrode material using a porous carbonaceous material are disclosed in Japanese Patent Laid-open Nos. 2003-217982, 2003-81624, 2002-373835, and the like, but each of the examples gives a lower capacity, as compared to those of electrochemical capacitors, which matters particularly in use for automobiles and the like.

15

Besides, in the case of using only the porous carbonaceous material for electrodes, it is necessary to add acetylene black or the like to the binder for the purpose of enhancing conductivity, but, even with such an addition, the interface resistance is very high, which constitutes a serious problem.

20

On the other hand, the electrochemical capacitors using a metal oxide uses a conductive metal oxide as above-described. Although such electrochemical capacitors have very high capacities as compared to the cases of using the above-mentioned porous carbonaceous material, the electrochemical capacitors are disadvantageous on the basis of production cost, since the metal of the metal oxide generally belongs to noble metals. For example, pseudo-capacity capacitors using a thin film of ruthenium oxide or indium oxide as electrode material have been reported to have an electrostatic

25

30

capacity of 160 F/cc in an aqueous system, in the 5th International Seminar on Double Layer Capacitors and Similar Energy Storage Device held in Florida, USA, in 1995.

5 Besides, the electrochemical capacitors using a conductive polymer material as electrode material generally show a much higher capacity, as compared with those of capacitors using the above-mentioned porous carbonaceous material, but their characteristics may vary depending on the method of forming the electrodes. For example, where the conductive polymer is deposited on collector plates by an electrolytic polymerization method as described in Japanese Patent Laid-open Nos.
10 Hei 6-104141 and Hei 6-104142, the capacitor has a capacity of 3.7 F and an internal resistance of 13.9 Ω , and the formation of electrodes by the electrolytic polymerization method generally involves a serious problem as to productivity thereof.

15 Therefore, many proposals have been made to use combinations of carbonaceous materials (mainly carbon black) and intrinsically conductive polymers. As described above, only two methods have been used to prepare such mixtures - a dry blending method of powders (by ball milling and the like) and the polymerisation of the conductive polymer in presence of the carbon black.

20 The method of synthesizing a conductive polymer by chemical oxidation polymerization and preparing a composite material from the conductive polymer and other conductive inorganic material is an apparently relatively simple technology for forming electrodes, and many examples of this technology have come to be made public in recent years. However, its reproducibility is poor and therefore, no such
25 mixtures are in practical use, because the problems to be overcome when trying to scale up and develop a reproducible process are huge.

For example, Japanese Patent Laid-open No. 2002-265598 discloses the use of a
30 composite material of an organic conductive oligomer and an inorganic material as electrode material. In this case, however, the organic conductive oligomer cannot be

expected to have a high conductivity, so that the inorganic material is required to have a very high conductivity in order to lower the internal resistance.

5 Besides, as a similar case of using a conductive polymer material, a method of polymerizing the conductive polymer in a porous carbonaceous material (Japanese Patent Laid-open No. 2001-210557) cannot produce a conductive polymer with a high conductivity but leads to an increase in the internal resistance of the capacitor.

10 As has been described above, there have hitherto been known a large number of examples of a capacitor using an electrochemically active conductive polymer or inorganic oxide. However, the use of the inorganic material leads to a problem as to production cost, whereas the use of the conductive polymer involves difficulties in control of conductivity, control of particle size and reproducibility, resulting in that the capacitors cannot show sufficient performance.

15

It was therefore the object of this invention to create a carbon material / conductive polymer mixture which allows a reproducible manufacturing and superior performance values especially for the manufacturing of supercapacitors.

20 [Detailed description of the invention]

Most surprisingly, a mixture of (intrinsically) conductive polymer(s) with carbon based materials, like carbon black, graphite, carbon nanotubes or fullerenes, can reproducibly be manufactured, if the conductive polymer(s) is (are) provided in
25 colloidal form and the colloidal form of conductive polymer is mixed with the carbon based material.

Preferred embodiments of the present invention are disclosed in the dependent claims.

30 One embodiment of the present invention resides in electrodes for a high-capacity capacitor comprising a porous carbonaceous material or a valve metal, at least one of

the electrodes being formed from a composition containing an electrochemically active substance, and the composition being prepared by dispersing primary particles of a conductive polymer dispersed in a liquid dispersion medium, wherein the primary particles have an average particle diameter of less than 500 nm and a specific surface area of more than 15 m²/g measured according to BET method. Particularly, the electrochemically active substance material is prepared by dispersing the conductive polymer in water or an organic solvent, and, particularly by controlling the particle size of the conductive polymer, it is possible to strongly bind the porous carbonaceous material and to form a stable electrode or electrodes. While a non-conductive organic binder has been used as a binder for binding the porous carbonaceous material in the prior art, the conductive material according to the invention makes it possible to form the electrode without using a binder. In addition, the adhesive force for adhesion to a collector plate can be sufficiently secured by controlling the particle diameter. As another effect, the dispersion of particulates of the conductive polymer makes it possible to enlarge the specific surface area necessary for the formation of an electrical double layer, and is very advantageous to impregnation with an electrolytic solution. The conductive polymer is not particularly limited, and examples thereof include polyaniline, polyaniline derivatives, polythiophene, polythiophene derivatives, polypyrrole, polypyrrole derivatives, polythianaphthene, polythianaphthene derivatives, polyparaphenylene, polyparaphenylene derivatives, polyacetylene, polyacetylene derivatives, polyparaphenylenevinylene, polyparaphenylenevinylene derivatives, polynaphthalene, and polynaphthalene polynaphthalene derivatives. The method for polymerizing the conductive polymers is not particularly limited, and the usable methods include electrolytic oxidation polymerization, chemical oxidation polymerization, and catalytic polymerization. The polymer obtained by the polymerizing method as mentioned is neutral and is not conductive per se. Therefore, the polymer is subjected to p-doping or n-doping. By the doping, the polymer can be made into a conductive polymer. The substance used for the doping is not particularly limited; generally, a substance capable of accepting an electron pair, such as a Lewis acid, is used. Examples of the substance include hydrochloric acid, sulfuric acid, organic sulfonic acid derivatives such as parasulfonic acid, polystyrenesulfonic acid,

alkylbenzenesulfonic acid, camphorsulfonic acid, alkylsulfonic acid, sulfosalicylic acid, etc., ferric chloride, copper chloride, and iron sulfate.

5 A further embodiment of the present invention pertains to the conductivity of the
conductive polymer, and contributes particularly to a reduction in the equivalent series
resistance of the capacitors. While it is a general practice to add acetylene black or
the like as a conductivity-imparting material in the case of an electrode for a capacitor
which uses a porous carbonaceous material, the material according to the invention is
10 characterized in that, by setting the conductivity to 100 S/cm or more, the conductive
polymer by itself has the function as a conductivity-imparting material, making it
unnecessary to especially add a conductivity-imparting material. Since it is
unnecessary to add a conductivity-imparting material, it is possible to enlarge the
capacity of the actual product. In this case, the conductivity of the conductive
polymer is necessarily at least 100 S/cm, preferably 200 S/cm or more, and more
15 particularly 500 S/cm or more. The conductivity is preferably as high as possible,
since it has a great influence on the internal resistance of the capacitor to be made.

20 A further embodiment of the present invention resides in an electrode composition for
a capacitor, wherein the conductive polymer is dispersed in water or an organic
solvent. Particularly, the composition specified conditionally can be used separately
for the case where the electrolyte in the capacitor is water and for the case where the
electrolyte is an organic solvent. Especially where the electrolytic liquid is water, the
use of the conductive polymer dispersed in an organic solvent is advantageous to
stability of the electrode.

25 A further embodiment of the present invention pertains to an electrode composition
for a capacitor, wherein the conductive polymer dispersion element contains solid
components in a concentration of not more than 20 wt%. Particularly at the time of
forming the electrodes, the concentration of the solid components greatly influences
30 the productivity and cost. However, the solid components in the conductive polymer
dispersion element influences the stability of the dispersion, too. Therefore, the

concentration of the solid components is not more than 20 wt% where production cost is taken into account, and the concentration is not more than 10 wt%, preferably not more than 5 wt%, where the stability of the dispersion is also taken into account.

5 A further embodiment of the present invention pertains to an oxidation-reduction reaction of the conductive polymer. Particularly where the stability attendant on a structural change arising from the chemical reaction is taken into consideration, setting of minimum proton movement has a good influence on the device life. Preferable examples of such a conductive polymer material include polyaniline,
10 polyaniline derivatives, polypyrrole, and polypyrrole derivatives.

A further embodiment of the present invention pertains to the specific surface area of the porous carbonaceous material. The present definition pertains to the capacity of the capacitor, and a sufficient capacity can be obtained by use of the carbonaceous
15 material with a specific surface area of not less than 100 m²/g, preferably 500 m²/g, more preferably 1000 m²/g. Such a porous carbonaceous material is dispersed in the conductive polymer dispersion element. In order to attain a highly dispersed state, the dispersing process can be carried out by use of an ordinary ball mill, a planetary ball mill, a homogenizer, or an ultrasonic dispersing apparatus. Where the planetary ball
20 mill is used, stirring is preferably carried out for at least 30 min. Stirring for a long time is attended by a trouble such as a rise in the temperature of the solvent; therefore, cooling is needed in the case of stirring for not less than 1 hour.

A further embodiment of the present invention pertains to the amount of the porous
25 carbonaceous material added. It is necessary to add the porous carbonaceous material in an amount of at least 5 wt%. The addition amount has a close relation with the charge-discharge rate of the capacitor. It is desirable to add the porous carbonaceous material in a larger amount in the case of devices required of quick charge-discharge, and to add the conductive polymer in a larger amount in the case of devices required
30 of slow charge-discharge. Thus, according to the present invention, it suffices to control the addition amount according to the device requirements. In order to obtain a

capacitor device with a capacity at least greater than that of a capacitor device using the porous carbonaceous material solely, it is necessary to add the conductive polymer in an amount in terms of solid components of not less than 5 wt%. In order to obtain a sufficient oxidation-reduction performance, it is necessary to add the conductive polymer in an amount in terms of solid components of preferably not less than 10 wt%.

10 A further embodiment of the present invention resides in electrodes for a capacitor, opposed to each other with the separator disposed therebetween, wherein both of the two electrodes are composed of the same kind of conductive polymer. This configuration has the merit of providing a very inexpensive device, in consideration of the productivity thereof.

15 A further embodiment of the present invention resides in electrodes for a capacitor, wherein the compositions used to form the two electrodes opposed to each other with the separator disposed therebetween are composed of different kinds of conductive polymers. This is based on the consideration of the general fact that many of organic conductive polymers show different activities under a positive voltage and under a negative voltage. In other words, a method of obtaining a high-capacity device
20 resides in using a conductive polymer material which shows the highest electrical activity when the voltage is swept.

A further embodiment of the present invention resides in electrodes for a capacitor, opposed to each other with the separator disposed therebetween, wherein one of the
25 two electrodes is formed of a porous carbonaceous material, and the other is composed of a porous carbonaceous material/conductive polymer composite body as defined herein. With this configuration, a high capacity can be expected in the case of using an intercalation electrode as the porous carbonaceous electrode.

30 A further embodiment of the present invention resides in electrodes for a capacitor, opposed to each other with the separator disposed therebetween, wherein one of the

two electrodes is formed of a metal oxide, and the other is composed of a porous carbonaceous material/conductive polymer composite body as defined herein. This configuration is effective particularly in the case of obtaining a high capacity by utilizing the oxidation-reduction characteristics of the metal oxide electrode.

- 5 Particularly desirable examples of the material of the metal oxide electrode are ruthenium oxide and indium oxide.

10 Besides, where the inorganic material/conductive polymer composite body in the present invention is formed into a film or other molded product, it is possible to add a stabilizer, a light stabilizer, a filler, a binder, a conductivity-imparting agent and the like, as required.

[Mode for Carrying Out the Invention]

15 Experimental Example 1: Production Method of Porous Carbonaceous Material/Conductive Polymer Composite Electrode

20 Pulverized coconut shell active carbon (not yet activated) in an amount of 18 g was dispersed in 90.9 g of a conductive polymer dispersion element (ORMECON 7301-026-002; solvent: xylene; solid components: 2.2%), and the mixture was stirred by a planetary ball mill for 60 min. To the porous carbonaceous material/conductive polymer slurry, 57.3 g of xylene was further added, and the mixture was stirred by a stirring motor for 30 min, to prepare a porous carbonaceous material/conductive polymer dispersion.

25

Electrodes for a capacitor need change of collector plates according to an electrolytic solution. In this experiment, platinum plates were used for electrodes in the case of using aqueous sulfuric acid solution (1 mol/l) as the electrolytic solution, and aluminum was used for the electrodes in the case of using propylene carbonate for the electrolytic solution. Where platinum is used for the collector plates in the actual electrodes for the capacitor, first, the surfaces of platinum plates are scratched with a

30

file, and are then coated with a fixed amount of the porous carbonaceous material/
conductive polymer dispersion prepared above. Then, the coated platinum plates are
placed in a high-temperature tank at 100°C for 1 hour to sufficiently remove the
organic solvent. The electrodes thus formed were subjected to weighing of the
5 electrode active substance, and were used directly as the electrodes for the capacitor.

10 Next, in the case of using a 1 mol/l solution of tetraethylammonium
tetrafluoroborate in propylene carbonate as an organic solvent based electrolytic
solution; aluminum plates were used as collector plates. The aluminum collector
plates were scratched by a file and coated with a fixed amount of the porous
carbonaceous material/conductive polymer dispersion, in the same manner as in the
case of using the platinum plates as the collector plates. Thereafter, drying was
conducted at 100°C for 24 hours, to sufficiently remove moisture.

15 The components of the dispersion element used for forming the porous
carbonaceous material/conductive polymer composite electrodes are shown in the
following table.

	Conductive polymer	Dispersion medium	Specific surface area of active carbon (m ² /g)	Solid component ratio C:ICP
Experimental Example 1	Polyaniline	Xylene	1100	9:1
Experimental Example 2	Polyaniline	Xylene	1100	8:2
Experimental Example 3	Polyaniline	Xylene	1100	1:9
Experimental Example 4	Polyaniline	Xylene	1600	9:1
Experimental Example 5	Polyaniline	Xylene	1600	8:2
Experimental Example 6	Polyaniline	Xylene	1600	1:9
Experimental Example 7	Polyaniline	Water	1600	8:2
Experimental Example 8	PEDOT	Water	1600	8:2

Experimental Example 2: Production of Capacitor Cell

- 5 Each electrode plate with the electrode active substance in close contact therewith prepared in Experimental Example 1 is blanked into circular disks with a diameter of 1 cm, to prepare two electrodes. A glass fiber filter is blanked into a circular shape with a diameter of 1.5 cm, and the circular product is used as a separator. Further, an aqueous 1 M solution of sulfuric acid is used as an electrolytic
- 10 solution in the case of an aqueous system. A 1 M solution of tetraethylammonium

tetrafluoroborate in propylene carbonate is used as an electrolytic solution in the case of an organic solvent system.

Evaluation of Capacitor Characteristics

Measuring Instruments: The internal resistance of each capacitor cell was measured by use of an impedance analyzer YHP 4192A. Measurements in a charge-discharge test were carried out by use of a TOYO System TOSCAT-3100U.

The results of the charge-discharge test of capacitors using the electrode active substances shown in Experimental Example 1 are shown as Examples in the following table.

Examples	Electrode active substance	Dispersion	Charging rate (mA/cm ²)	Charging capacity (F/g)	Discharging rate (mA/cm ²)	Discharging capacity (F/g)
Example 1	Experimental Example 1	Sulfuric acid solution	10	250	10	250
Example 2	Experimental Example 1	Sulfuric acid solution	5	240	5	240
Example 3	Experimental Example 1	Sulfuric acid solution	1	220	1	220
Example 4	Experimental Example 2	Sulfuric acid solution	10	250	10	250
Example 5	Experimental Example 2	Sulfuric acid solution	5	220	5	220
Example 6	Experimental Example 2	Sulfuric acid solution	1	170	1	170
Example 7	Experimental Example 2	TEATFB	10	90	10	90
Example 8	Experimental Example 2	TEATFB	5	100	5	100
Example 9	Experimental Example 2	TEATFB	1	150	1	150
Example 10	Experimental Example 4	TEATFB	10	40	10	40

Example 11	Experimental Example 4	TEATFB	5	170	5	170
Example 12	Experimental Example 4	TEATFB	1	170	1	170
Example 13	Experimental Example 5	TEATFB	10	140	10	140
Example 14	Experimental Example 5	TEATFB	1	200	1	200
Example 15						
Example 16						
Example 17						
Example 18						
Example 19						
Example 20						
Example 21						
Example 22						
Example 23						
Example 24						

The results of evaluation of internal resistance are shown in Figure 1 and Figure 2. Measurement was conducted by use of a capacitor cell formed by using the electrodes using the dispersion elements of Example 2 and Example 5, and using a 1 M sulfuric acid solution as the electrolytic solution.

Fig. 1 shows the internal resistance of the capacitor using the porous carbonaceous material with a specific surface area of $1600 \text{ m}^2/\text{g}$.

5 Fig. 2 shows the internal resistance of the capacitor using the porous carbonaceous material with a specific surface area of $1100 \text{ m}^2/\text{g}$.

Comparative Example:

[Effects of the Invention]

10 As has been described above, the present invention provides an electrical double layer capacitor in which a pair of polarizable electrodes each comprising a solid electrolyte of a conductive polymer contained in an active carbon layer are opposed to each other with a separator disposed therebetween. Particularly, by enhancing the particle diameter and conductivity of the conductive polymer, it is possible to obtain
15 an electrical double layer capacitor having a low internal resistance and a high capacity.

Claims

1. A composition capable of forming a coating and comprising a mixture of a conductive polymer in colloidal form and carbon.
2. The composition according to claim 1, wherein the conductive polymer is selected from polymers of anilines, thiophenes, pyrroles and substituted derivatives thereof.
3. The composition according to claim 1 or claim 2, wherein two or more different conductive polymers are present.
4. The composition according to any one of the preceding claims, wherein the carbon has a specific surface area of more than $100 \text{ m}^2/\text{g}$, as measured according to the BET method.
5. The composition according to any one of the preceding claims, wherein the carbon is selected from graphite, carbon black, nanotubes and fullerenes.
6. The composition according to claim 5, wherein the carbon is active carbon black.
7. The composition according to claim 6, wherein the active carbon black has a specific surface of greater than $750 \text{ m}^2/\text{g}$.
8. The composition according to any one of the preceding claims, wherein the average particle size (number average) of the conductive polymer is smaller than 500 nm.
9. The composition according to any one of the preceding claims, wherein the conductivity of the conductive polymer is greater than 10^{-5} S/cm .

10. The composition according to claim 9, wherein the conductivity is greater than 10 S/cm.
11. The composition according to claim 10, wherein the conductivity is greater than 100 S/cm.
12. The composition according to any one of the preceding claims, wherein the weight ratio of the conductive polymer to carbon is in the range of from 1 : 50 to 50 : 2.
13. The composition according to any one of the preceding claims, further comprising a liquid dispersion medium in a concentration of from 40 to 99.5 weight percent, wherein the dispersion medium liquid is evaporable under ambient conditions, and other non-evaporable additives in a concentration of from 0 to 10 weight percent, the conductive polymer and carbon components being present in a concentration of from 0.5 to 60 weight percent, all weight percentages being based on the total composition.
14. The composition according to claim 13, wherein the liquid dispersion medium comprises water and/or organic solvent(s).
15. A method for manufacture of a composition according to any one of the preceding claims, comprising dispersing the conductive polymer and carbon, and optionally additives in a liquid dispersion medium and optionally drying the liquid dispersion after application on a substrate.
16. The method of claim 15, wherein the conductive polymer is dispersed in a first liquid and the carbon is dispersed separately in a second liquid, said liquids being the same or different, and the respective dispersions are subsequently mixed together, optional additives being added before, during or after the separate dispersion steps.

17. The method of claim 15, wherein the conductive polymer is dispersed in a liquid and the carbon is separately milled in the absence of liquid, and wherein the dry milled carbon is subsequently added to the liquid colloidal dispersion of the conductive polymer and dispersed therein.
18. A composite material comprising the composition according to any one of claims 1 to 14 or the composition obtained by the method of any one of claims 15 to 17 in the form of a coating on a substrate.
19. The composite material of claim 18, wherein the substrate is selected from the group consisting of metals, semiconductors, plastics, ceramics and wood products.
20. An electrical or electronic article comprising the composition according to any one of claims 1 to 14 or the composite material according to claim 18 or claim 19.
21. The article of claim 20, wherein the article is selected from the group consisting of conductors, energy stores, sensors, switches, condensers, capacitors and supercapacitors, double layer capacitors and redox capacitors.
22. The article of claim 21, said article being a capacitor comprising an electrolyte and a pair of electrodes with a separator disposed therebetween, wherein at least one of the electrodes comprises the composition according to any one of claims 1 to 14 or the composite material according to claim 18 or claim 19.
23. The capacitor of claim 22, wherein both electrodes comprise the composition according to any one of claims 1 to 14 or the composite material according to claim 18 or claim 19.

24. The capacitor of claim 22, wherein one electrode comprises the composition according to any one of claims 1 to 14 or the composite material according to claim 17 or claim 18 and the other electrode is a conventional capacitor electrode.
25. The capacitor of claim 24, wherein the other electrode comprises a current collector coated with a composition containing an intrinsically conductive polymer but no carbon.

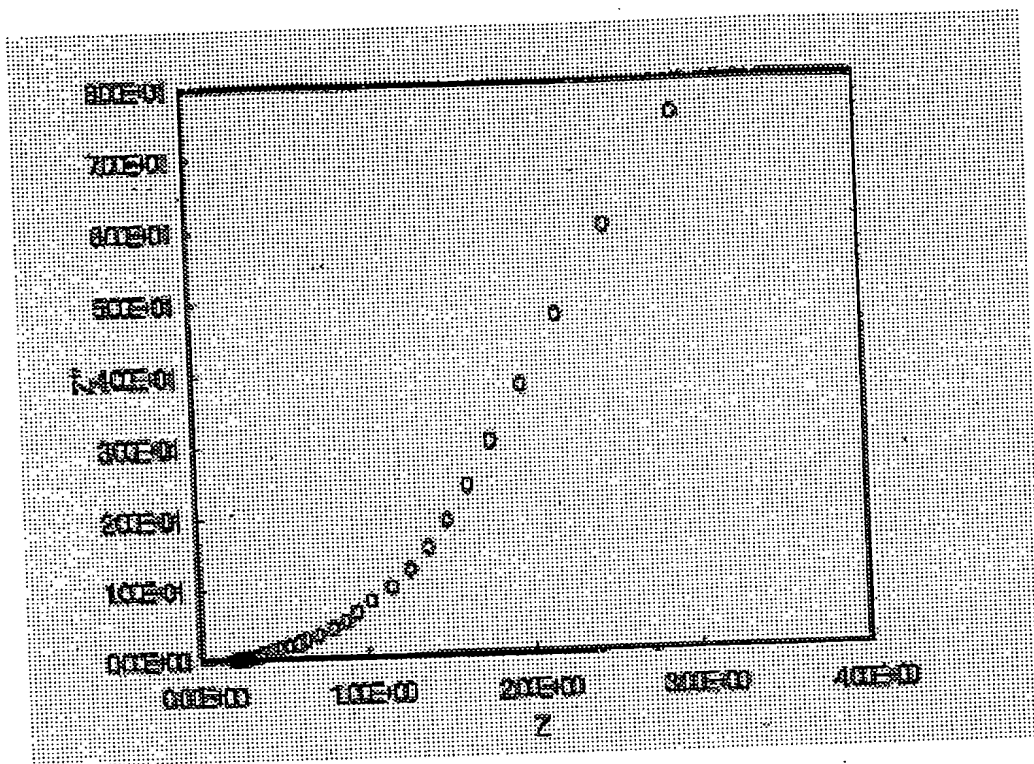


FIGURE 1

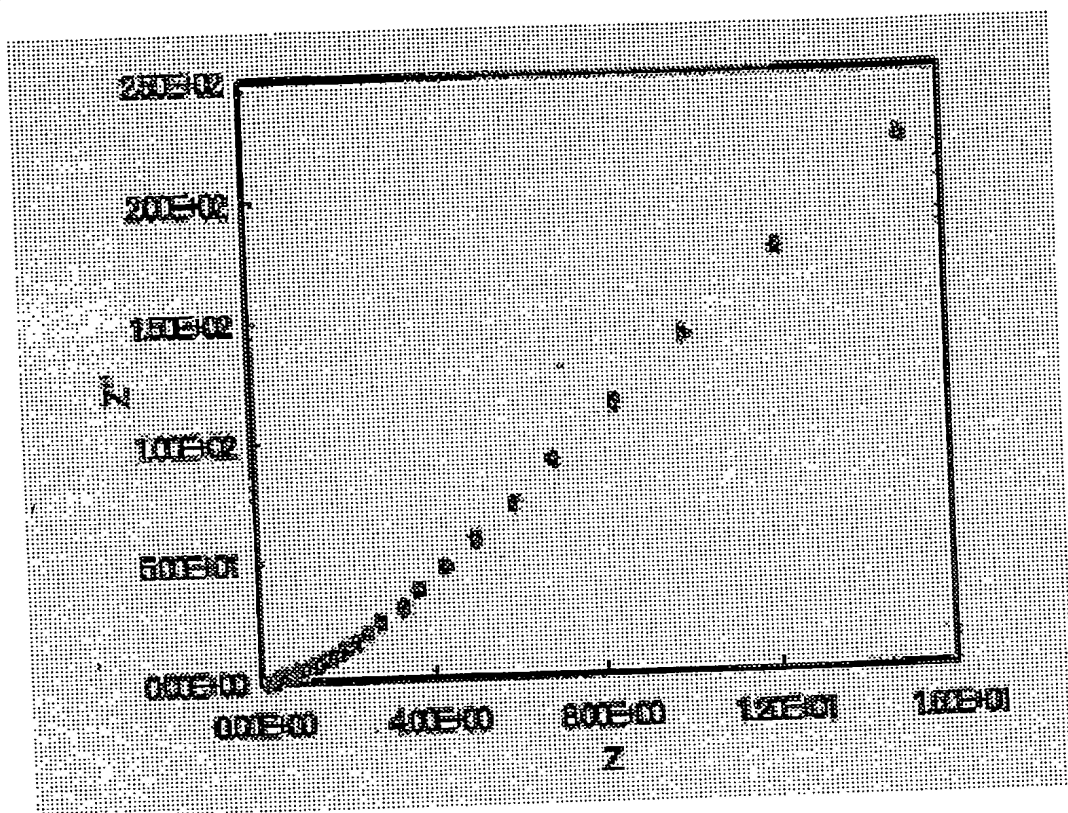


FIGURE 2

From the INTERNATIONAL BUREAU

PCTNOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

NOHLEN, Martin
Uexküll & Stolberg
Beselerstrasse 4
22607 Hamburg
ALLEMAGNE

Date of mailing (day/month/year) 06 May 2005 (06.05.2005)	
Applicant's or agent's file reference P 68146	IMPORTANT NOTIFICATION
International application No. PCT/EP05/002889	International filing date (day/month/year) 17 March 2005 (17.03.2005)
International publication date (day/month/year)	Priority date (day/month/year) 18 March 2004 (18.03.2004)
Applicant ORMECON GMBH et al	

1. By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt by the International Bureau of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. (If applicable) The letters "NR" appearing in the right-hand column denote a priority document which, on the date of mailing of this Form, had not yet been received by the International Bureau under Rule 17.1(a) or (b). Where, under Rule 17.1(a), the priority document must be submitted by the applicant to the receiving Office or the International Bureau, but the applicant fails to submit the priority document within the applicable time limit under that Rule, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
3. (If applicable) An asterisk (*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b) (the priority document was received after the time limit prescribed in Rule 17.1(a) or the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b)). Even though the priority document was not furnished in compliance with Rule 17.1(a) or (b), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
18 March 2004 (18.03.2004)	10 2004 013 634.3	DE	26 April 2005 (26.04.2005)
19 March 2004 (19.03.2004)	10 2004 014 021.9	DE	26 April 2005 (26.04.2005)
29 April 2004 (29.04.2004)	60/566,954	US	26 April 2005 (26.04.2005)

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Aumaitre Chantal

Facsimile No. +41 22 740 14 35

Facsimile No. +41 22 338 70 80
Telephone No. +41 22 338 8669